

MULTIUSE, SOLID CLEANING DEVICE AND COMPOSITION

CROSS-REFERENCED RELATED APPLICATIONS

[0001] This application is a continuation-in-part of United States Patent Application No. 10/775,264, filed February 10, 2004 entitled "Autonomous Cleaning Composition And Method." This application is also a continuation-in-part of United States Patent Application No. 10/925,331, filed August 24, 2004 entitled "Multiuse, Solid Cleaning Device And Composition." Both of these applications are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to a multiuse, solid cleaning composition. More specifically, the present invention is drawn to compositions for cleaning with water, including slow release compositions which provide consistent concentrations of cleaning agents delivered into water over multiple wash cycles.

[0003] Chemical cleaning agents, in one form or another, have long been used to remove dirt, oil, and particulate matter from a wide variety of articles. Cleaning improves the visual and tactile impression of an article, kills potentially harmful microbes, removes particles that interfere with breathing and vision, and may even extend the life of the article being cleaned. Things such as cookware, homes, automobiles, clothing, and the human body itself stand to benefit from the development of enhanced cleaning agents. Although the present invention contemplates cleaning systems useful for cleaning a wide variety of articles, it is particularly well-adapted for cleaning clothes, as in a washing machine.

[0004] Soaps and detergents are two of the most common cleaning agents presently used. While they are often used interchangeably, the words "soap" and "detergent" actually denote different classes of compounds.

[0005] Soaps are made by a process of saponification wherein a fatty acid reacts with a base to yield the salt of the fatty acid, *i.e.*, a soap. Soap probably has its origin in reacting animal fats, or lard, with alkaline salts, such as wood ash. Today, they are largely synthesized from animal fats and plant oils. Molecules of soap owe their cleaning capacity to their amphiphilic structure, which includes a hydrophobic portion consisting of a long hydrocarbon chain, and a hydrophilic portion composed of an ionic group at one end of the hydrocarbon chain. Because of the hydrocarbon chain, a molecule of soap is not truly soluble in water. Numerous molecules of soap will suspend in water as micelles, or clusters of molecules with

long hydrocarbon chains in the inner portions of the cluster, and ionic, water soluble ends facing the polar water.

[0006] Because these micelles form hydrophobic centers, they are able to dissolve other non-polar substances, like oils. Once the non-polar, oily dirt is dissolved within the micelles of soap, the ionic surfaces of the micelle repel each other, suspending the oil droplets and preventing them from coalescing. In this fashion, dirt and oil become trapped within the water soluble micelles, and wash away with the water.

[0007] A primary disadvantage of soaps is that they form insoluble salts (precipitates) with ions found in hard water. These salts, usually formed when Ca^{++} and Mg^{++} ions react with the carboxylate ends of soap molecules, precipitate out of solution as bathtub rings, grits, and other deposits. Water softeners that exchange Ca^{++} and Mg^{++} ions for more soluble Na^+ ions can alleviate most of this problem.

[0008] Most laundry products and many household cleansers actually contain detergents, not soaps. A detergent is a compound with a hydrophobic hydrocarbon chain plus a sulfonate or sulfate ionic end (whereas soaps have carboxylic ends). Because detergents also have an amphiphilic structure, they also form micelles and clean in the same fashion as soaps. However, detergents have the advantage that most metal alkylsulfonates and sulfates are water-soluble. Therefore, detergents do not precipitate out of solution with metal ions found in water. As a result, detergents are not inhibited by hard water. In addition, detergents can be synthesized with continuous chain alkyl groups, which are more easily broken down, or biodegraded, into smaller organic molecules by the microorganisms in septic tanks and sewage treatment plants.

[0009] A drawback of most detergents is that they contain additives that take much longer to biodegrade. Some components containing phosphates must be treated in plants. Phosphates promote algae growth, choking bodies of water and streams. Another disadvantage of detergents is that they can leave behind an undesirable residue even after thorough rinsing.

[0010] Detergents are currently used in many household appliances, such as dishwashers and washing machines. Presently, a user must measure out a dose of detergent to add to the cleaning appliance before every cleaning cycle. Conventional packaging and use of detergents creates messy clutter, consumes time, and typically results in a waste of detergent from overdosing. In addition, most washing machines for clothing use a separate rinsing

cycle in order to remove the residue. Thus, additional time, water, and heat energy are required to complete the washing process.

[0011] It would be a great advancement in the art to provide a novel cleaning system that uses a novel non-detergent composition of cleaner that leaves no residue and therefore, requires no rinsing cycle. Another improvement in the art would be to provide a cleaning agent that is biodegradable. Still another improvement would be if this cleaning agent were made from natural materials. It would also be a great advancement in the art to provide a new method for making a non-detergent cleaning agent. It would be another advancement in the art to provide a cleaning agent that cleans as good as or better than the detergents presently on the market.

[0012] Furthermore, it would be an improvement in the art to simplify the cleaning process and ameliorate the resultant mess with improved, preferably measurement-free or automatic, dosing over many cleaning cycles.

BRIEF SUMMARY OF THE INVENTION

[0013] In accordance with the invention as embodied and broadly described herein, a multiuse, solid cleaning device and cleaning method are disclosed in suitable detail to enable one of ordinary skill in the art to make and use the invention.

[0014] The multiuse cleaning device contains a homogeneous quantity of cleaning agent in solid form configured to slowly dissolve and release a substantially consistent quantity of cleaning agent over a plurality of wash and rinse cycles. The device may be used in various cleaning applications such as laundry and dish washing applications.

[0015] The cleaning agent includes a gas-releasing component, a solubility control component to limit the solubility of the cleaning agent, an alkalinity agent as a pH regulator, a water softener to solvate metal ions in a solution of water, and an optical brightener for increased color clarity and brightness. Gas-releasing component clean by reacting with acids (soils) and by mechanical microscrubbing as they yield gases, such as carbon dioxide. The gas-releasing component is preferably selected from carbonates, bicarbonates, perborates, percarbonates, and mixtures thereof. Sodium perborate monohydrate, sodium percarbonate, sodium bicarbonate, sodium carbonate, and mixtures thereof are presently preferred gas-releasing agents.

[0016] The solubility control agent is a material resistant to dissolving in water, i.e., water insoluble or slightly water-soluble. It controls solubility by dissolving only an equilibrium

concentration of composition in solution. The amount of solubility control component in the composition determines the equilibrium concentration of the composition in a solution, e.g., water. Therefore, the amount of solubility control component should be sufficient to yield a predetermined equilibrium concentration of the cleaning agent. Similarly, the amount of cleaning agent should be sufficient to provide a predetermined amount of gas in solution. The amount of alkalinity agent should be sufficient to provide a predetermined pH in solution. The amount of water softener should be sufficient to soften household water in solution.

[0017] U.S. Patent Nos. 6,178,987, 6,262,004, and 6,403,551 disclose a solid cleaning composition containing amorphous silica as the solubility control agent. Amorphous silica (H_2SiO_3) is a preferred solubility control agent because it occurs in nature and is completely biodegradable. In the cleaning compositions containing amorphous silica disclosed in the above-identified patents, careful heating and pressurizing are needed to prepare the cleaning compositions. It has been found that commercially available potassium silicate ($\text{K}_2\text{O} \cdot n\text{SiO}_2 \cdot m\text{H}_2\text{O}$), in liquid form, may be used to prepare the cleaning agent compositions at room temperature without special heating or pressure. Other silicates, such as sodium silicate, tend to dissolve quickly and may not provide desired solubility control. However, in some cases sodium silicate may be usable within the scope of the present invention. The other ingredients may be used at approximately the same concentration reported in the foregoing patents. Completion of the process may include casting or molding the composition in a shape selected to control surface area, and curing the composition. The composition cures independently at room temperature as water becomes depleted through evaporation and/or as a result of the anhydrous compounds absorbing water.

[0018] The water softener is preferably a naturally occurring and biodegradable material capable of solvating hard water ions, such as a zeolite. Naturally occurring zeolites are presently preferred; however, the invention may be used with synthetic zeolites which function in a manner equivalent to natural zeolites and which biodegrade. The water softener solvates hard ions and inhibits them from reacting with other components to form insoluble salts.

[0019] The cleaning agent preferably include an optical brightener present in an amount from about 0.5 to 8 % by weight, more preferably from about 0.5 to 5 % by weight, and optimally from about 0.5 to 3 % by weight. The cleaning agent may optionally include a fragrance component present in an amount from about 0.5 to 12 % by weight, more preferably

from about 1 to 12 % by weight, and optimally from about 1 to 5 % by weight. The cleaning agent may optionally include an anti-redeposition component present in an amount from about 0.5 to 10 % by weight, more preferably from about 0.5 to 5 % by weight, and optimally, from about 0.5 to 3 % by weight.

[0020] The alkalinity agent is present in an amount sufficient to give a solution of the composition a pH greater than 7, and preferably a pH from about 7 to about 10.5, more preferably from 7.8 to about 8.8. Examples of alkalinity agents include, but are not limited to, an alkali hydroxide, alkali hydride, alkali oxide, alkali sesquicarbonate, alkali carbonate, alkali phosphate, alkali borate, alkali salt of mineral acid, alkali amine, alkaloid, alkali cyanide, and mixtures thereof. Sodium hydroxide is one presently preferred alkalinity agent.

[0021] In certain embodiments within the scope of the present invention, the method of preparing the solid cleaning agent may include providing a solvent, such as water; providing a gas-releasing agent, such as sodium bicarbonate, sodium percarbonate, sodium perborate monohydrate, sodium perborate tetrahydrate, and mixtures thereof; providing a water softener, such as a zeolite; providing a solubility control agent, such as potassium silicate; mixing the ingredients; pouring the mixture into a curing vessel; and allowing the composition to cure to a solid form.

[0022] A porous covering or bag may be disposed around the solid cleaning agent to hold it during use. The porous covering or bag may optionally be elastic and conform to the size of the solid cleaning agent as the cleaning agent shrinks in size due to dissolution of cleaning agent. The covering or bag helps reduce or eliminate direct transfer of cleaning agent residue onto fabric surfaces after a final rinse cycle when the cleaning device and fabric surfaces are in contact for an extended time period. The porous covering or bag may be an elastic net-like material or a woven fabric material. It may be a porous fabric bag with a covering of ruffle-like material.

[0023] The bag houses or surrounds the cleaning agent may also be used in conjunction with the present invention. The bag may also be configured to retain fragrance with the cleaning agent, to create more sudsing (lathering) during agitation of the washing machine, to create drag in the water to quiet any contact with the agitator/cleaning agent and the tub of the washing machine, and/or to create a barrier between the cleaning agent and the clothes (which prevents or reduces discoloration of the clothes).

[0024] In some embodiments, the bag is a multilayered structure. In further embodiments, the bag is made of three layers: an outer layer, a middle layer, and an inner layer. The outer

and inner layers may be both made of a porous material through which water may pass. In some embodiments, this porous material is a mesh material that is smooth and non-abrasive. The middle layer may be constructed to provide spacing and/or padding between the outer layer and the inner layer. In some embodiments, the middle layer is made of a material such as ruffled netting and porous foam.

[0025] The cleaning device may include a indicator structure disposed within the quantity of cleaning agent to signal when to replace the cleaning device. It may optionally include an internal skeleton within the quantity of cleaning agent to provide structural strength to the cleaning device.

[0026] The ball may be spherical, aspherical, oval, oblate, rounded, or irregular shaped. The cleaning device is preferably in the form of a ball. The size of the cleaning device may vary depending upon the concentration of the cleaning agent and its dissolution rate and the desired quantity of cleaning agent to be released in each wash or rinse cycle. For example, a more concentrated cleaning agent, with a slower dissolution rate, may have a smaller size than a device having a lower concentration cleaning agent with a higher dissolution rate. For convenience, the cleaning device may have a diameter in the range from about 2 to about 6 inches in residential applications and 4 to 12 inches in commercial/industrial applications. A device having a size approximately the same as a softball may be used.

[0027] The cleaning agent in solid form dissolves and releases a substantially consistent quantity of cleaning agent over from about 5 to 50 (or more) laundry wash or rinse cycles. In other embodiments, the cleaning agent in solid form dissolves and releases a substantially consistent quantity of cleaning agent over from about 10 to 40 laundry wash or rinse cycles. As would be expected, the choice to use hot, warm, or cold water in the wash/rinse cycle will affect the dissolution of the cleaning agent—*i.e.*, the cleaning agent will more readily dissolve in hot water than in cold water. Thus, the exact number of wash/rinse cycles that the cleaning agent will be operable will depend in part on the temperature of the water in the washing machine.

[0028] Similarly, the weight of the solid cleaning agent will affect the number of wash or rinse cycles. For example, a 600 gram device is expected to provide more cleaning cycles than a 300 gram device.

[0029] As noted above, the cleaning agent 10 is designated such that a substantially consistent quantity of cleaning agent 10 will dissolve during each laundry cycle. “Substantially consistent quantity” means that the amount of cleaning agent that dissolves per

wash cycle generally will fall within a predictable range. For example, the range may be defined as follows:

$$\overline{X}_{10} \pm \text{about } 50 \%$$

where \overline{X}_{10} is the average amount of cleaning agent that dissolves during the first 10 wash cycles and “50 %” means 50 % of the \overline{X}_{10} value. However, embodiments in which the amount of cleaning agent 10 that dissolves per wash cycle may range as high as $\overline{X}_{10} \pm$ about 65 %. Some of the presently preferred embodiments will be designed such that the amount of cleaning agent 10 that dissolves per wash cycle is within the range $\overline{X}_{10} \pm$ about 40 % and even $\overline{X}_{10} \pm$ about 25 %.

[0030] In one embodiment of the cleaning agent within the scope of the present invention, the gas-releasing component is present in an amount from about 20 % to 60 % by weight, the solubility control component is present in an amount from about 20 % to 60 % by weight, the water softener is present in an amount from about 0.5 % to 20 % by weight, the alkalinity agent is present in an amount from about 0.5 % to 20 % by weight, and the optical brightener is present in an amount from about 0.5 % to 8 % by weight.

[0031] In a preferred embodiment within the scope of the present invention, the gas-releasing component is present in an amount from about 40 % to 55 % by weight, the solubility control component is present in an amount from about 35 % to 50 % by weight, the water softener is present in an amount from about 1 % to 10 % by weight, the alkalinity agent is present in an amount from about 1 % to 12 % by weight, and the optical brightener is present in an amount from about 0.5 % to 5 % by weight.

[0032] In a more preferred embodiment within the scope of the present invention, the gas-releasing component is sodium perborate monohydrate present in an amount from 42% to 52% by weight, the solubility control component is potassium silicate present in an amount from 35% to 45% by weight, the water softener is a zeolite present in an amount from 1% to 5% by weight, the alkalinity agent is sodium hydroxide present in an amount from 1% to 5% by weight, and the optical brightener is present in an amount from about 0.5 % to 3 % by weight.

[0033] A method of providing laundry cleaning agent to a laundry cleaning machine is disclosed. The method includes the step of obtaining a multiuse laundry cleaning device in a

solid state containing a homogeneous quantity of cleaning agent in solid form configured to dissolve and release a substantially consistent quantity of cleaning agent over a plurality of laundry wash and rinse cycles. As mentioned above, the cleaning device may have a porous covering or bag disposed around the solid cleaning agent. The porous covering or bag may be elastic and conform to the size of the solid cleaning agent as the cleaning agent shrinks in size due to dissolution of cleaning agent. The porous covering or bag may be pliable and may not necessarily conform to the size of the solid cleaning agent. The method further includes the step of depositing the laundry cleaning device within the laundry cleaning machine tub under conditions such that the laundry cleaning device is exposed to water from the plurality of laundry wash and rinse cycles.

[0034] These and other features, and advantages of the present invention will become more fully apparent from the following description and appended claims, or may be learned by the practice of the invention as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] Figure 1 shows a multiuse cleaning device within the scope of the present invention.

[0036] Figure 2 shows a cross-sectional view of a multiuse cleaning device.

[0037] Figure 3 shows a cross-sectional view of another multiuse cleaning device.

[0038] Figure 4 shows a perspective view of a bag that houses the multiuse cleaning device.

[0039] Figure 5 is a cross-sectional view taken along the line A-A of Figure 4.

[0040] Figure 6 is a graph of cleaning agent released per load for the results reported in Table 2C.

[0041] Figures 7A-7G are graphs of cleaning agent released per load for the results reported in Tables 7A-7G.

DETAILED DESCRIPTION OF THE INVENTION

[0042] The present invention is drawn to a multiuse cleaning device containing a homogeneous quantity of cleaning agent in solid form and to methods of manufacture and use. The cleaning agent in solid form preferably provides controlled dissolution in contact with water such that a sufficient quantity of cleaning agent is dissolved and released for use in multiple wash cycles of a cleaning appliance.

[0043] The cleaning agent composition may include a gas-releasing agent that is water soluble, and a solubility control agent that is only slightly water soluble. The gas-releasing agent provides cleaning action. However, if the gas-releasing agent is permitted to freely dissolve, the resulting cleaning solution will have an unknown or uncontrolled concentration of gas-releasing agent. Thus, it is desirable to add a solubility control agent to the cleaning agent to control its equilibrium concentration, and hence, the concentration of gas-releasing agent in the cleaning solution.

[0044] The cleaning agent may be further enhanced through the addition of an alkalinity agent and a water softener. The alkalinity agent controls the pH of the cleaning agent, and therefore the pH of the resultant cleaning solution. The pH of the cleaning solution preferably remains within a certain range because the pH controls the rate at which the gas-releasing agent reacts. The gas-releasing agent or the solubility control agent may be configured to control the pH of the cleaning solution, but a separate alkalinity agent is presently preferred. The softener prevents the formation of a residue on the items to be cleaned by solvating hard water ions. The gas-releasing agent, the solubility control agent, or the alkalinity agent may be configured to solvate hard water ions, but a separate softener is preferable.

[0045] The gas-releasing agent should not release gas in the solid state cleaning agent, but it should be able to release gas in a cleaning solution of the cleaning agent at ambient temperature. The gas-releasing agent need not react with other agents, but may simply decompose at ambient temperature to release gas. Those gas-releasing compounds that are natural and biodegradable are preferred. In some embodiments, the gas-releasing agent is a carbonate, bicarbonate, percarbonate, or perborate. For example, sodium percarbonate, which is also known as sodium carbonate peroxyhydrate, ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$), sodium bicarbonate, (NaHCO_3), sodium perborate monohydrate ($\text{NaBO}_3 \cdot \text{H}_2\text{O}$), sodium perborate tetrahydrate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$), and sodium carbonate (Na_2CO_3) are effective, low cost gas-releasing agents. Mixtures of gas releasing agents may be used. However, numerous other gas-releasing agents are known to those skilled in the art, and all are within the scope of the present invention. Sodium perborate monohydrate is a presently preferred gas releasing agent.

[0046] The solubility control agent should be either water insoluble or only slightly water soluble. Numerous compounds may serve this function, including but not limited to hydrophobic compounds. Those solubility control agents that are both found in nature and biodegradable are preferred. Potassium silicate is presently preferred because it may be used to prepare the solid cleaning agent composition at room temperature.

[0047] The alkalinity agent may be selected from, but is not limited to, a group consisting of alkali hydroxide, alkali hydride, alkali oxide, alkali carbonate, alkali bicarbonate, alkali phosphate, alkali borate, alkali salt of mineral acid, alkali amine, alkaloid, alkali cyanide, alkali metal, and alkali earth metal. Sodium hydroxide is an example of one presently preferred alkalinity agent. Other alkalinity agents that tend to increase the pH of a neutral solution are familiar to those in the art, and are within the scope of the present invention. Those alkalinity agents that are both found in nature and biodegradable are preferred. Sodium carbonate provides the dual function of an alkalinity agent and a gas releasing agent. Potassium silicate may provide the dual function of an alkalinity agent and a solubility control agent. Similarly, sodium percarbonate provides alkalinity control in addition to its gas release function. In addition to being an alkalinity agent, sodium hydroxide may provide the dual function of being an a processing aid that facilitates the formation of a potassium silicate slurry and/or provides catalytic action for solidification of the cleaning agent.

[0048] The softener should preferably be selected to exchange soluble sodium or other ions for the insoluble calcium and magnesium ions. Those softeners that are both found in nature and biodegradable are preferred. A cleaning agent composition wherein the softener is natural zeolite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_x \cdot (\text{H}_2\text{O})_x$) is presently preferred because it occurs in nature and is completely biodegradable. Synthetic zeolites may be used provided that they perform the desired softening function and are biodegradable.

[0049] The amount of gas-releasing agent in the cleaning agent determines how much gas is released in a cleaning solution of the cleaning agent formed when the cleaning agent dissolves in a solvent, e.g., water. Therefore, the gas-releasing agent in the cleaning agent should comprise an amount sufficient to release a predetermined amount of gas in a cleaning solution of the cleaning agent. A concentration of gas-releasing agent from 20% to 60% by weight of the cleaning agent may be used, with a concentration from 40% to 55% being more preferred. In one embodiment, the concentration of gas-releasing agent is from 42% to 52% by weight.

[0050] The amount of solubility control agent in the cleaning agent determines the equilibrium concentration of the cleaning agent in the cleaning solution. Therefore, the amount of solubility control agent in the cleaning agent should be selected to yield a predetermined equilibrium concentration of cleaning agent in the cleaning solution. A concentration of solubility control agent from 20% to 60% by weight of the cleaning agent

may be used, with a concentration from 35% to 50% being more preferred. In one embodiment, the concentration of solubility control agent is about 35% to 45% by weight.

[0051] The amount of alkalinity agent in the cleaning agent affects the pH of the cleaning solution. Therefore, the cleaning agent should include an amount of alkalinity agent selected to provide a cleaning solution within a predetermined pH range. A concentration of alkalinity agent from 0.5% to 20% by weight of the cleaning agent may be used, with a concentration from 1% to 12% by weight being more preferred. Because the alkalinity agent may also provide gas releasing functionality, in the case of sodium carbonate, the actual concentration of the gas releasing agent and alkalinity agent may be outside the foregoing concentration range. In one embodiment, the concentration of alkalinity agent is about 1% to 5% by weight, providing a cleaning solution with a pH of about 8.8 after dilution inside the cleaning appliance.

[0052] The softener in the cleaning agent softens the cleaning solution by scavenging residue-forming ions. Therefore, the softener should comprise an amount of cleaning agent sufficient to soften household water. A concentration of softener from 0.5% to 20% by weight of the cleaning agent may be used, with a concentration from 1% to 10% being more preferred. In one embodiment, the concentration of the softener is about 1% to 5% by weight.

[0053] The optical brightener is an additive that improves visual appearance in cleaned fabrics. Optical brighteners are known to persons having ordinary skill in the art. An optical brightener may be added to the cleaning agent in an amount from about 0.5% to 8% by weight, and more preferably from about 0.5% to 5% by weight. In one embodiment, the concentration of optical brightener is about 0.5% to 3% by weight. One currently preferred optical brightener is sold under the tradename Tinopal by Ciba Specialty Chemicals, Inc. of Basel, Switzerland.

[0054] Water molecules may form complexes with these components and could be bound up within the cleaning agent by virtue of the process of making the cleaning agent. Water may comprise from 1% to 50% of the cleaning agent by weight. Preferably, water comprises approximately 20% by weight of the cleaning agent. It will be appreciated that some components of the cleaning agent may contain water, such as potassium silicate, sodium perborate monohydrate, sodium hydroxide, zeolite, and other ingredients, which may limit the amount of extra water that needs to be mixed with the dry ingredients.

[0055] In operation, items to be cleaned are exposed to the cleaning solution, which causes a number of processes occur. The basic cleaning solution attacks the acids in dirt and oil.

The gas-releasing agent releases gas that reacts with dirt and oil. In a cleaning appliance for washing clothing, dirt and oil would be dislodged from clothing in a removal step due to reaction with the released gas. The gas-releasing agent provides a sustained release of gas that continues to react with removed soils.

[0056] Simultaneously, in a scavenging step, the softener scavenges ions to prevent the buildup of residue on the articles to be cleaned. In addition, the alkalinity agent keeps the pH of the cleaning solution slightly basic. This serves two functions. First of all, it limits the reaction of the gas-releasing agent so that the gas evolves at a controlled rate and the cleaning solution has time to become thoroughly intermixed with the articles to be cleaned. Second, the basic cleaning solution reacts to neutralize acids in the soils.

[0057] An exemplary cleaning process utilizing an exemplary cleaning agent will now be described. First, the sodium percarbonate and sodium carbonate attack acids within the dirt and oils. The acid-base reactions have an emulsifying affect on the dirt and oils. Particularly, sodium percarbonate (which includes sodium carbonate) reacts with acids to generate carbon dioxide in an acid and base reaction: $2\text{H}^+(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow 2\text{Na}^+(\text{aq}) + \text{H}_2\text{O} + \text{CO}_2(\text{g})$. Most oils and dirt found in clothing are slightly acidic, and so the sodium carbonate component of the percarbonate may react with these dirt and oils to produce carbon dioxide. This tiny explosion of gas, as it bubbles out of solution, dislodges the dirt from clothes and other materials, allowing it to be washed away. The reaction yields sodium ions in solution, or the sodium salts of the oils and dirt of the reaction, water and carbon dioxide.

[0058] In this embodiment, the byproducts of the cleaning process appear in nature, so there is no need for the extensive treatment of phosphates and other non-biodegradable materials, as required by presently available detergents. However, the alkalinity agent, which may include sodium carbonate, is added primarily to increase the pH of the cleaning solution but also functions as a gas releasing agent, described above. In a similar manner, sodium percarbonate, is added primarily as a gas releasing agent but also increases the pH of the cleaning solution as an alkalinity agent.

[0059] The alkalinity agent provides a mildly basic solution to prevent the sodium percarbonate from reacting with excess hydrogen ions (H^+) in aqueous solution. Without the alkalinity agent, CO_2 would bubble out of solution too quickly as the sodium percarbonate reacts with random hydrogen ions. With a slightly alkaline cleaning solution, in one embodiment approximately 8.5 to 10 pH, the sodium percarbonate reacts at a controlled rate, and preferably with the acids in the dirt and oils.

[0060] The softener, which may be natural or synthetic zeolite, exchanges sodium ions (Na^+) for magnesium (Mg^{++}) and calcium (Ca^{++}) ions: $\text{Mg}^{++} + \text{Ca}^{++} + \text{zeolite} \rightarrow \text{zeolite} + 4\text{Na}^+$. Sodium ions and sodium salts are readily water soluble and will not form precipitates. Without the softener, the Mg^{++} and Ca^{++} could react to form insoluble salts, precipitating out of solution and leaving a hard film behind, as shown by the following equations: $\text{NaHCO}_3 + \text{Mg}^{++} \rightarrow \text{MgCO}_3$, and $\text{NaHCO}_3 + \text{Ca}^{++} \rightarrow \text{CaCO}_3$.

[0061] One possible method for making the cleaning agent in a solid state will be described. In the described method a solvent, a gas releasing agent, a solubility control agent, an alkalinity agent, and a softener, are combined to form the cleaning agent. It will be appreciated that the cleaning agent may be manufactured with some components performing multiple functions or with additional, unnamed agents.

[0062] The solvent may be included with the solubility control agent, if in liquid form. The solvent will typically be water, and may comprise from 1% to 50% by weight of the cleaning agent composition.

[0063] Referring to Figure 1, a multiuse cleaning device 10 is illustrated. The cleaning device 10 is shown in the form of a spherical ball. The ball does not need to be spherical, but it can take any practical, easily manufactured shape such as aspherical, oval, oblate, rounded, or other irregular shaped configuration.

[0064] As shown in Figure 2, the multiuse cleaning device 10 contains a homogeneous quantity of cleaning agent 12 in solid form. The cleaning agent 12 has a composition as described herein. In the embodiment shown in Figure 2, the cleaning device 10 is a solid mass of cleaning agent. The cleaning device is deposited within the laundry cleaning machine tub under conditions such that the laundry cleaning device is exposed to water from the plurality of laundry wash and rinse cycles. Under typical conditions, the cleaning device is deposited within the tub or wash basin together with the soiled clothing, towels, linens, and similar articles (hereinafter referred to as "laundry articles"), to be laundered. Water from wash and rinse cycles dissolves a portion of the cleaning device and releases a controlled quantity of cleaning agent which is able to clean the laundry articles as described herein. Upon completion of the cleaning cycle, the clean laundry articles are removed, but the cleaning device may remain within the laundry cleaning machine tub for use in multiple cleaning cycles.

[0065] Referring to Figure 3, the cleaning device 10 may have an indicator structure 16 which indicates when it is time to replace a used cleaning device with a fresh cleaning device

10. The structure 16 may take a variety of different forms. For example, it may spherical, disk, rod, spiked, or irregular shaped. The important feature is that the structure be able to indicate, such as by a visible sign, that the cleaning device 10 should be replaced. The cleaning device 12 may include a support structure or internal skeleton disposed within the quantity of cleaning agent 12 to provide structural strength to the cleaning device.

[0066] Also shown in Figure 3 is a porous covering or bag 14 disposed around the solid cleaning agent 12. The porous covering or bag 14 may be elastic and conform to the size of the solid cleaning agent 12 as the cleaning agent shrinks in size due to dissolution of cleaning agent 12. The porous covering or bag 14 may be pliable or flexible and not necessarily conform tightly to the cleaning agent as it dissolves and shrinks in size. The covering 14 helps reduce or eliminate direct transfer of cleaning agent residue onto fabric surfaces after a final rinse cycle when the cleaning device and fabric surfaces are in contact for an extended time period. For example, users do not always remove laundry articles from the laundry cleaning machine as soon as the wash cycle is completed. Under such circumstances, the cleaning device 10 would contact moist fabric surfaces for a period of time. This may result in transfer of cleaning agent onto fabric surfaces. The porous covering or bag 14 provides a barrier which separates the cleaning agent 12 from the fabric surfaces. The covering 14 may be a net-like material or a woven fabric material. The covering 14 may include ruffles on the outer surface to create a greater separation distance between the cleaning agent 12 and clean or moist fabric surfaces.

[0067] Referring now to Figure 4, an embodiment of the bag 14 is illustrated in greater detail. As explained in greater detail above, the bag 14 is designed such that it may surround and/or house the cleaning agent 10. In general, the bag 14 has a top end 80 and a bottom end 82. The bottom end is 82 sealed through sewing, stitching, Velcro, elastic, bonding, or other similar methods. The top end 80 comprises a closeable top 86 such that the bag 14 may surround and house the agent 10. In some embodiments, the closeable top 86 is a drawstring. However, Velcro, elastic, or other items/methods capable of forming a closeable top may also be used.

[0068] Figure 4 also shows a graphical illustration of pores or openings 90 that may be part of the material used to make the bag 14. Such pores 90 are added to all or a portion of the bag 14 and are designed to allow water to pass through the bag 14 but to retain the solid cleaning agent 10. As noted above, the pores 90 may be formed by using a woven fabric material, a net-like material, or other materials. In one presently preferred embodiment, the

bag 14 is made from material of the type used to make athletic jerseys, such as football jerseys. This material not only has adequate porosity to freely allow the passage of water, but also this type of material is non-abrasive to the other laundry articles in the washing machine.

[0069] Figure 5 is a cross-sectional view taken along the line A-A of Figure 4 and illustrates the construction of the bag 14. The bag 14 may comprise multiple layers of material. In general, these multiple layers of material are used so that when the bag 14 surrounds the agent 10, there is about ½ inch of material between the agent 10 and the laundry articles in the washing machine. In the embodiment shown in Figure 5, three distinct layers of material have been used. Other embodiments may also be made using more or less than three layers, as desired.

[0070] In Figure 5, the porous bag 14 includes an outer layer 100, a middle layer 102, and an inner layer 104 which have been connected together via stitching 106. Of course, other methods of connecting the layers together such as bonding with adhesive or heat, weaving, etc. may also be used. In some embodiments, it may be important to select materials for the layers 100, 102, 104 that (1) allow the water freely pass in and out of the bag 14 and (2) will not retain more than negligible amounts of water.

[0071] The outer layer 100 and the inner layer 104 may be both made of a porous material, such as a mesh material. However, the outer layer 100 and the inner layer 104 need not be made of the same material. They may be made of different materials. The outer layer 100 is preferably smooth and non-abrasive to the clothing or other laundry articles. The inner layer 104 may be smooth and non-abrasive to the cleaning device to minimize unwanted mechanical abrasion of the cleaning agent.

[0072] The middle layer 102 is made of a padding material to provide spacing and/or structure between the outer layer 100 and the inner 104. The middle layer may be constructed of materials such as ruffled netting, porous foam, or other similar materials.

[0073] In further embodiments, the bag 14 may also be configured such that it performs one or more of the following functions:

[0074] (1) retains fragrance with the cleaning agent;

[0075] (2) creates more sudsing (lather) during agitation of the washing machine;

[0076] (3) creates drag in the water to quiet any contact with the agitator/cleaning agent and the tub of the washing machine;

[0077] (4) retains fragments of the cleaning agent;

[0078] (5) creates a barrier between the cleaning agent and the clothes (which prevents/reduces discoloration of the clothes); and/or

[0079] (6) provides a more consistent dissolution rate of the cleaning device over multiple wash/rinse cycles.

[0080] Of course, the bag 14 may perform other functions depending on factors such as the construction of the bag, the size of the bag, etc.

[0081] EXAMPLES:

[0082] The following examples are given to illustrate various embodiments within the scope of the present invention. These are given by way of example only, and it is to be understood that the following examples are not comprehensive or exhaustive of the many embodiments within the scope of the present invention.

[0083] Example 1

[0084] A cleaning agent composition was prepared by mixing the dry ingredients listed in Table 1A with the wet ingredients listed in Table 1B:

[0085] Table 1A:

<u>Dry Ingredients</u>	<u>Weight (g)</u>	<u>Weight Percent</u>
Sodium perborate monohydrate	230 g	45.5
Optical brightener	5 g	1.0
Antiredeposition agent	5 g	1.0
Zeolite	15 g	3.0
Fragrance	22 g	2.2
Total:	267 g	52.7

[0086] Table 1B:

<u>Wet Ingredients</u>	<u>Weight (g)</u>	<u>Weight Percent</u>
Potassium Silicate	201 g	39.8
Sodium hydroxide	9 g	1.8
Surfactant	29 g	5.7
Total:	239 g	47.3

[0087] After the foregoing ingredients are mixed, the mixture is poured into a mold and allowed to cure and solidify.

[0088] Example 2

[0089] A multiuse laundry cleaning device in a solid state was prepared by molding cleaning agent having the formula of Example 1 into a spherical ball. The spherical ball was placed inside a washing machine tub and subjected to repeated wash cycles in the washing machine tub. Additional multiuse laundry cleaning devices were prepared and tested in several different types of commercially available washing machines. Wash cycles ranged from delicate to regular to heavy duty, and different water temperature settings were used. The multiuse laundry cleaning device remained in the washing machine tub for both wash and rinse cycles. After the cleaning cycles were complete, the cleaning device was removed from the washing machine and weighed to determine the quantity of cleaning agent that was dissolved during the preceding wash cycle. Representative results from two tests are reported in Tables 2A and 2B.

[0090]Table 2A

<u>Wash Cycle</u>	<u>Cleaning Device Weight (g)</u>	<u>Cleaning Agent Released</u>
0	422	
1	394	28
2	336	58
3	283	53
4	231	52
5	189	42
6	164	25
7	129	35
8	99	30
9	76	23
10	64	12
11	44	20
12	35	9
13	30	5
14	27	3
15	21	6

Table 2B

<u>Wash Cycle</u>	<u>Cleaning Device Weight (g)</u>	<u>Cleaning Agent Released</u>
0	435	
1	389	46
2	335	54
3	283	52
4	236	47
5	206	30
6	171	35
7	145	26
8	134	11
9	124	10
10	102	22

[0091] The average amount of cleaning agent released per wash cycle in Table 2A over 10 wash cycles was 35.8 g. The average amount of cleaning agent released per wash cycle in Table 2B over 10 wash cycles was 33.3.

[0092] Results from a test with more wash cycles are reported in Table 2C below:

[0093] Table 2C

<u>Wash Cycle</u>	<u>Cleaning Device Weight (g)</u>	<u>Cleaning Agent Released</u>
0	430	
1	401	29
2	366	35
3	336	30
4	306	30
5	281	25
6	252	29
7	238	14
8	218	20
9	193	25
10	179	14
11	157	22
12	137	20
13	122	15
14	103	19
15	78	25
16	64	14
17	46	18
18	31	15
19	11	20

[0094] The average amount of cleaning agent released per wash cycle in Table 2C over 19 wash cycles was 22.1 g. A graph of the results shown in Table 2C, grams of cleaning agent released per wash cycle load, is shown in Figure 6.

[0095] One cleaning agent composition within the scope of the invention has the following ingredients set forth in Table 3:

[0096] Table 3

<u>Ingredient</u>	<u>Weight Percent</u>
Water	29%
Sodium Bicarbonate	39%
Natural Zeolite	8%
Potassium silicate	21%
Sodium Sesquicarbonate	3%

[0097] Another cleaning agent composition within the scope of the present invention has the following ingredients set forth in Table 4:

[0098] Table 4

<u>Ingredient</u>	<u>Weight Percent</u>
Sodium Perborate	
Monohydrate	37.0%
Sodium Carbonate	31.2%
Natural Zeolite	8%
Optical Brightener	1.0%
Potassium silicate	22.8%

[0099] With the formula of Table 4, ingredients were added as listed. The powders (first four items) were combined and mixed prior to adding liquid potassium silicate. After adding the potassium silicate, the product was mixed briefly and poured into a mold. Set-up and hardening began within twenty minutes after the addition of the potassium silicate at room temperature.

[00100] The sodium perborate monohydrate and the sodium carbonate both release gas. The carbonate releases carbon dioxide and the perborate releases oxygen. The potassium silicate provides some solubility control. The sodium carbonate serves a dual role as gas releaser and alkalinity agent.

[00101] It has been found that potassium silicate may be used successfully, while sodium silicate is noticeably less-effective to prepare the cleaning agent. While not being bound by theory, it is believed that potassium silicate is operative because it does not raise the pH too high and does not dissolve in water as readily as sodium silicate. Potassium silicate has a pH of about 11, whereas sodium silicate has a pH of about 13. With this information, it may be possible to include a suitable pH modifier with sodium silicate to successfully prepare the cleaning agent.

[00102] Yet another cleaning agent composition within the scope of the present invention has the following ingredients set forth in Table 5:

[00103] Table 5

<u>Ingredient</u>	<u>Weight Percent</u>
Sodium Percarbonate	38%
Sodium Carbonate	25%
Carboxymethylcellulose	1%
Natural Zeolite	8%

Potassium silicate 28%

[00104] With the formula of Table 5, ingredients were added as listed. The powders (first four items) were combined and slowly mixed to minimize dusting, but mixed briskly enough to ensure total dispersion. The liquid potassium silicate was added slowly with the mixer running. As the product thickens, a small amount of base (sodium hydroxide, less than 0.5 weight percent) was added to aid in processing by thinning the material and allowing a longer mix time. After about 5 to 10 minutes, the product started to stiffen, and it was poured into a mold for curing. Set-up and hardening began within ten minutes after the addition of the potassium silicate at room temperature.

[00105] The carboxymethylcellulose is a soil anti-redeposition compound. The sodium percarbonate and the sodium carbonate both release gas. The carbonate releases carbon dioxide and the percarbonate releases oxygen. The potassium silicate provides some solubility control. The sodium carbonate serves a dual role as gas releaser and alkalinity agent. The amounts listed in Table 4 can be varied by a few weight percent.

[00106] Another cleaning agent composition within the scope of the present invention has the following ingredients set forth in Table 6:

[00107] Table 6A

<u>Dry Ingredients</u>	<u>Weight Percent</u>
Gas-releasing Agent	43.7 %
Antiredeposition Agent	1.0%
Optical brightener	1.0%
Natural Zeolite- 40 mesh	3.2%
Fragrance-linen	3.0%

[00108] Table 6B

<u>Wet Ingredients</u>	<u>Weight Percent</u>
Surfactant	1.9%
Potassium silicate	43.7%
Sodium hydroxide—25%	2.5%

[00109] The cleaning agent disclosed in Table 6 is made in accordance with the procedures of Example 1 outlined above. The amounts listed in Table 6 can be varied by a few weight percent.

[00110] In Table 6, the anti-redeposition agent was carboxymethylcellulose. The gas-releasing agent was sodium perborate monohydrate. The potassium silicate provides some solubility control. The alkalinity agent was sodium hydroxide. The optical brightener was Tinopal, which is made and available from the Ciba Specialty Chemicals, Inc. The surfactant was Calsoft F-90, which is available from the Pilot Chemical Co.

[00111] Additional tests were also done regarding the dissolution of the cleaning agent in the washing machine. In these tests, the laundry cleaning device remained in the washing machine tub for both wash and rinse cycles. After the cleaning cycles were complete, the cleaning device was removed from the washing machine and weighed to determine the quantity of cleaning agent that was dissolved during the preceding wash cycle. Representative results from two tests are reported in Tables 7A-7G.

[00112] Table 7A

Wash Cycle	Cleaning Device Weight (g)	Cleaning Agent Released (g)
0	430	0
1	430	35
2	395	30
3	365	30
4	335	25
5	310	29
6	281	14
7	267	20
8	247	25
9	222	14
10	208	22
11	186	20
12	166	15
13	151	19
14	132	25
15	107	14
16	93	18
17	75	15
18	60	20
19	40	40

[00113] The average amount of cleaning agent released per wash cycle in Table 7A over 19 wash cycles was 22.6 grams. A graph of the results shown in Table 7A, grams of cleaning agent released per wash cycle load, is shown in Figure 7A.

[00114] Results from another test with more wash cycles are reported in Table 7B below. These tests were done with a warm wash and a cold rinse cycle.

[00115] Table 7B

Wash Cycle	Cleaning Device Weight (g)	Cleaning Agent Released (g)
0	680	0
1	680	13
2	667	13
3	654	13
4	641	11
5	630	14
6	616	19
7	587	20
8	567	25
9	542	14
10	528	12
11	516	13
12	503	15
13	488	17
14	471	11
15	460	14
16	446	18
17	428	15
18	413	20
19	393	9
20	384	6
21	378	11
22	367	10
23	357	10
24	347	9
25	338	11
26	327	16
27	311	14
28	297	13
29	284	10
30	274	15
31	259	16
32	243	22
33	221	17
34	204	12
35	192	9

36	183	17
37	166	20
38	146	15
39	131	13
40	118	15
41	103	8
42	95	10
43	85	13
44	72	6
45	66	4
46	62	

[00116] The average amount of cleaning agent released per wash cycle in Table 7B over 46 wash cycles was 13.2 grams. A graph of the results shown in Table 7B, grams of cleaning agent released per wash cycle load, is shown in Figure 7B.

[00117] Results from yet another test with more wash cycles are reported in Table 7C below. These tests were done with a cold wash and a cold rinse cycle.

[00118] Table 7C

Wash Cycle	Cleaning Device Weight (g)	Cleaning Agent Released (g)
0	680	0
1	680	14
2	666	11
3	655	9
4	646	10
5	636	9
6	627	8
7	619	7
8	612	8
9	604	12
10	592	6
11	586	5
12	581	8
13	573	11
14	562	5
15	557	8
16	549	13
17	536	8
18	528	7
19	521	10
20	511	8
21	503	7
22	496	11
23	485	13

24	472	8
25	464	7
26	457	7
27	450	8
28	442	10
29	432	9
30	423	9
31	414	7
32	407	8
33	399	12
34	387	11
35	376	9
36	367	10
37	357	11
38	346	10
39	336	10
40	326	9
41	317	6
42	311	5
43	306	7
44	299	10
45	289	8
46	281	9
47	272	10
48	262	12
49	250	9
50	241	14
51	227	8
52	219	9
53	210	10
54	200	7
55	193	7
56	186	6
57	180	10
58	170	11
59	159	7
60	152	7
61	145	5
62	140	6
63	134	12
64	122	10
65	112	8
66	104	6
67	98	10
68	88	12
69	76	9
70	67	9
71	58	8
72	50	9

73	41	8
74	33	8
75	25	

[00119] The average amount of cleaning agent released per wash cycle in Table 7C over 75 wash cycles was 8.7 grams. A graph of the results shown in Table 7C, grams of cleaning agent released per wash cycle load, is shown in Figure 7C.

[00120] It is important to note that even though a smaller amount of cleaning agent dissolved in the cold water tests shown in Table 7C, the dissolved cleaning agent in these tests was at least as effective in cleaning the laundry articles as detergents currently available and used in cold water. However, the use of the cleaning agent in exclusively cold water did increase significantly the longevity of the cleaning agent supply. In fact, these results indicate that, in cold water, the cleaning agent may provide adequate results in upwards of 70 wash/rinse cycles.

[00121] Results from a further test with multiple wash cycles are reported in Table 7D below. These tests were done with using lower density wash loads using a cold wash and a cold rinse cycle.

[00122] Table 7D

Wash Cycle	Cleaning Device Weight (g)	Cleaning Agent Released (g)
0	450	0
1	438	12
2	425	13
3	414	11
4	400	14
5	390	10
6	378	12
7	365	13
8	354	11
9	343	11
10	333	10
11	319	14
12	306	13
13	297	9
14	286	11
15	274	12
16	260	14
17	249	11
18	239	10
19	230	9

20	218	12
21	205	13
22	193	12
23	183	10
24	171	12
25	160	11
26	152	8
27	142	10
28	130	12
29	122	8
30	109	13
31	98	11
32	88	10
33	79	9
34	71	8
35	61	10
36	55	6
37	44	11
38	36	8
39	30	6
40	24	6

[00123] The average amount of cleaning agent released per wash cycle in Table 7D in 40 wash cycles was 10.6 grams. A graph of the results shown in Table 7D, grams of cleaning agent released per wash cycle load, is shown in Figure 7D.

[00124] Results from a further test with multiple wash cycles are reported in Table 7E below. These tests were done with using higher density wash loads using a cold wash and a cold rinse cycle.

[00125] Table 7E

Wash Cycle	Cleaning Device Weight (g)	Cleaning Agent Released (g)
0	450	0
1	442	8
2	433	9
3	425	8
4	418	7
5	408	10
6	400	8
7	392	8
8	385	7
9	379	6
10	372	7
11	363	9

12	355	8
13	345	10
14	338	7
15	332	6
16	324	8
17	319	5
18	312	7
19	304	8
20	296	8
21	287	9
22	280	7
23	275	5
24	266	9
25	259	7
26	251	8
27	245	6
28	235	10
29	226	9
30	218	8
31	211	7
32	204	7
33	193	11
34	184	9
35	176	8
36	166	10
37	160	6
38	155	5
39	147	8
40	137	10
41	128	9
42	121	7
43	115	6
44	106	9
45	99	7
46	91	8
47	83	8
48	77	6
49	72	5
50	67	5
51	61	6

[00126] The average amount of cleaning agent released per wash cycle in Table 7E in 51 wash cycles was 7.6 grams. A graph of the results shown in Table 7E, grams of cleaning agent released per wash cycle load, is shown in Figure 7E.

[00127] Results from a further test with multiple wash cycles are reported in Table 7F below. These tests were done with using lower density wash loads using a warm wash and a wash rinse cycle.

[00128] Table 7F

Wash Cycle	Cleaning Device Weight (g)	Cleaning Agent Released (g)
0	450	0
1	432	18
2	409	23
3	388	21
4	369	19
5	347	22
6	323	24
7	301	22
8	280	21
9	263	17
10	243	20
11	224	19
12	202	22
13	184	18
14	163	21
15	149	14
16	131	18
17	112	19
18	90	22
19	73	17
20	59	14
21	48	11
22	38	10

[00129] The average amount of cleaning agent released per wash cycle in Table 7F in 22 wash cycles was 18.7 grams. A graph of the results shown in Table 7F, grams of cleaning agent released per wash cycle load, is shown in Figure 7F.

[00130] Results from a further test with multiple wash cycles are reported in Table 7G below. These tests were done with using higher density wash loads using a warm wash and a wash rinse cycle.

[00131] Table 7G

Wash Cycle	Cleaning Device Weight (g)	Cleaning Agent Released (g)
0	450	0

1	434	16
2	419	15
3	401	18
4	389	12
5	375	14
6	364	11
7	352	12
8	337	15
9	325	12
10	315	10
11	297	18
12	284	13
13	274	10
14	262	12
15	248	14
16	230	18
17	211	19
18	197	14
19	175	22
20	163	12
21	146	17
22	134	12
23	124	10
24	113	11
25	103	10
26	90	13
27	82	8
28	73	9
29	63	10
30	56	7
31	48	8
32	39	9

[00132] The average amount of cleaning agent released per wash cycle in Table 7G in 32 wash cycles was 18.7 grams. A graph of the results shown in Table 7G, grams of cleaning agent released per wash cycle load, is shown in Figure 7G.

[00133] The present invention may be embodied in other specific forms without departing from its structures, methods, or other essential characteristics as broadly described herein and claimed hereinafter. The described embodiments are to be considered in all respects only as illustrative, and not restrictive. The scope of the invention is, therefore, indicated by the appended claims, rather than by the foregoing description. All changes that come within the meaning and range of equivalency of the claims are to be embraced within their scope.